# Full Articles

## Determination of isothermic compressibility of solvent from changes in the absorbance of a dye solution under pressure

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A new method of determination of the isothermic compressibility coefficient of a solvent from a change in the absorbance of a solution of the dye under elevated pressure (up to 100 MPa) was proposed. The method was checked by comparison with the known data for carbon tetrachloride and toluene at 25 °C.

**Key words:** compressibility, toluene, tetrachloromethane, high pressure.

Compressibility of the liquid and isothermic coefficient ($\beta$) are fundamental characteristics reflecting the change in the energy balance of the intermolecular attraction and repulsion with the pressure increase[1,2]

$$\beta = -(\partial V/\partial P)_T/V. \quad (1)$$

Data on a change in the liquid volume determined in temperature and pressure intervals make it possible to describe the ratio of the main thermodynamic parameters ($P$, $V$, $T$). Knowing the dependence of the $\Delta V/V$ value on pressure ($P$), one can calculate the change in the molar concentration under elevated pressure and refine the pressure effect on the rate and equilibrium of chemical processes. The change in the partial molar volume of compounds in solution is determined by differences in both the solvation energies and the ability of the solvent to be compressed in the solvate sphere.[1—5] For strong interactions the compressibility of the liquid results in negative values of the partial molar volume. Taking into account the compressibility of the medium, one can understand why the degree of bond dissociation upon its cleavage increases with the pressure increase, which often accelerates catalytic reactions.[3,4]

$$H_2O = H^+ + OH^- \ (\Delta V = -22.07 \text{ cm}^3 \text{ mol}^{-1})$$

The authors[6] attempted to find a relationship between the $\beta$ values and a set of other physical characteristics of a liquid, such as the thermal expansion coefficient ($\alpha_P$), molar volume ($V$), enthalpy ($\Delta_{vap}H$), and free energy of vaporization ($\Delta_{vap}G$). We extended the set of physical parameters of the liquid including the fraction of cavities upon molecular packing in the solvent $(V - V_W)/V$ taking into account the van der Waals volume ($V_W$) and a series of additional parameters; however, no reliable correlation

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was observed. It can be assumed that β depends on other properties of the liquid, which are not reflected in the listed characteristics.

Different approaches to direct experimental estimation of the compressibility of the liquid can be reduced to finding the pressure dependence of $\Delta V/V$. For this purpose different methods of measuring the volume, density, and ultrasonic speed for the adiabatic $\beta_S$ value or by gravimetry in the medium of the liquid under pressure[1—4] are used. The description of curved plots of $\Delta V/V$ *vs.* $P$ by a set of power equations is usually less accurate than semilogarithmic Tait´s equation[1]

$$\Delta V/V = C\ln[(B + P)/B], \qquad (2)$$

where $C$ and $B$ are constants for each liquid at a certain temperature.

Especially high differences are observed for derivatives of these functions under low excess pressure, which corresponds to different $\beta_0$ values. Analysis of the known methods for processing the dependence of $\Delta V/V$ on excess pressure showed[2] that for organic liquids in the pressure interval below 100 MPa the following linear equation should be considered the best:

$$V_0P/(V_0 - V_P) = 1/\beta_0 + mP, \qquad (3)$$

where $m$ is the proportionality factor for this liquid. Considerable errors in estimation of the $V_0P/(V_0 - V_P)$ values were shown[2] to be observed at low pressures (below 10—20 MPa) because of low accuracy of measurements of the $V_0 - V_P$ value. This can be caused by air microbubbles in the system or elevated compressibility of dissolved air, and the influence of these factors decreases sharply with the pressure increase. Equation (3) turned out to be simple and reliable for description of the experimental data on compressibility in an interval of 20—100 MPa and for their verification at 0—20 MPa.

We found that, unlike Eq. (3) that is fulfilled for an individual liquid, a distinct linear dependence between the tangent bulk modulus value at excess pressure close to zero, *viz.*, $K_0 = 1/\beta_0 = -V/(\partial P/\partial V)_T$, and an inverse compressibility value at 100 MPa ($-1000V/\Delta V$) is observed for different compounds. This dependence covers liquids of different classes (including alcohols, ethylene glycol, water, and even mercury) in a wide temperature interval (Table 1).

Since volume changes at 100 MPa are rather high and measured with high accuracy, the reliable (Fig. 1) method for checking and prediction of $\beta_0$ values appears for different compounds in a wide temperature range.

$$K_0 = (-4433.03\pm48.81) + (0.9872\pm0.0012)(1000V/\Delta V) \qquad (4)$$

$(R = 0.9999, \mathrm{SD} = 286.59, N = 47)$

**Table 1.** Isothermic compressibility coefficients under excess pressure close to zero ($\beta_0$/bar$^{-1}$) and the relative change in the volume of the liquid ($\Delta V/V_0$) at 100 MPa

| Compound | $T$/°C | $\beta_0\cdot10^6$ | $\Delta V/V_0\cdot10^4$ | $\Delta\beta/\beta_0\cdot100$* (%) |
|---|---|---|---|---|
| Dichloromethane | 25 | 102.6 | 693.4 | 0.67 |
| Chloroform | 25 | 103.3 | 693.8 | 1.36 |
| Tetrachloromethane | 25 | 108.9 | 715.0 | 1.24 |
| *n*-Hexane | 0 | 132.1 | 826.1 | −0.75 |
| | 25 | 162.9 | 946.2 | −2.16 |
| | 40 | 185.4 | 1026 | −3.83 |
| | 60 | 222.2 | 1142 | −6.50 |
| | 0 | 119.6 | 772.5 | −0.08 |
| | 25 | 144.4 | 876.0 | −1.18 |
| | 40 | 161.8 | 942.3 | −2.16 |
| | 60 | 189.1 | 1038 | −3.81 |
| *n*-Octane | 0 | 101.2 | 687.9 | 0.35 |
| | 25 | 121.4 | 780.7 | 0.52 |
| | 40 | 135.3 | 839.5 | −0.78 |
| | 60 | 157.7 | 927.1 | −1.97 |
| | 25 | 96.6 | 664.3 | −0.49 |
| | 45 | 113.1 | 742.0 | 0.34 |
| | 65 | 134.7 | 831.1 | 0.31 |
| Chlorobenzene | 25 | 75.1 | 551.5 | 1.13 |
| | 45 | 85.4 | 607.5 | 0.92 |
| | 65 | 97.6 | 669.2 | 0.86 |
| | 85 | 112.3 | 738.3 | 0.44 |
| Bromobenzene | 25 | 66.8 | 504.3 | 0.05 |
| | 45 | 75.2 | 552.1 | 1.15 |
| | 65 | 85.0 | 605.1 | 1.02 |
| | 85 | 96.4 | 663.3 | 0.80 |
| Nitrobenzene | 25 | 50.8 | 406.5 | 1.00 |
| | 45 | 55.9 | 438.3 | 1.21 |
| | 65 | 62.3 | 478.0 | 1.05 |
| | 85 | 69.8 | 522.4 | 1.06 |
| Aniline | 25 | 47.1 | 383.2 | 0.52 |
| | 45 | 52.1 | 414.6 | 0.84 |
| | 65 | 58.4 | 453.9 | 1.10 |
| | 85 | 65.6 | 497.4 | 1.22 |
| Acetone | 25 | 132.4 | 818.2 | 1.09 |
| 1,1-Dichloroethane | 25 | 113.4 | 757.3 | −2.19 |
| 1,2-Dichloroethane | 25 | 78.8 | 576.6 | −1.15 |
| 1,1,2,2-Tetrachloroethane | 25 | 61.7 | 478.8 | 0.07 |
| *trans*-1,2-Dichloroethylene | 25 | 111.9 | 738.8 | 0.08 |
| Trichloroethylene | 25 | 85.7 | 632.2 | −4.12 |
| Tetrachloroethylene | 25 | 79.1 | 563.2 | 3.63 |
| Water | 25 | 45.8 | 398.0 | −6.70 |
| Mercury | 25 | 4.0 | 38.8 | 0.00 |
| Ethylene glycol | 25 | 37.2 | 316.0 | −0.27 |
| Methanol | 25 | 124.8 | 809.1 | −3.03 |
| Ethanol | 25 | 115.3 | 730.2 | 4.81 |
| Propan-1-ol | 25 | 102.6 | 675.0 | 4.57 |

* Calculated from the ratio $100(\beta_0^{\mathrm{exp}} - \beta_0^{\mathrm{calc}})/\beta_0^{\mathrm{exp}}$, where $\beta_0^{\mathrm{calc}}$ was calculated by Eq. (4).

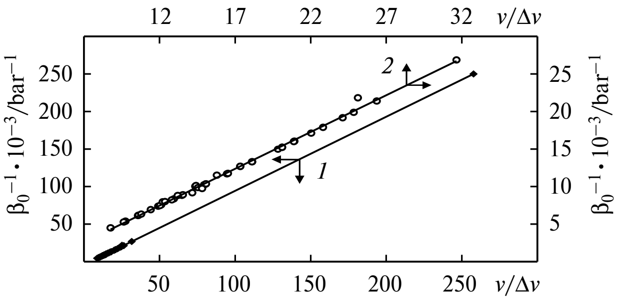

**Fig. 1.** Ratio between the tangent bulk modulus under excess pressure close to zero $K_0 = 1/\beta_0 = -V/(\partial P/\partial V)_T$ and the inverse compression value at 100 MPa ($V/\Delta V$) for all compounds presented in Table 1 (*1*, Eq. (4)) and ignoring the data for mercury (*2*, Eq. (5)).

If mercury that differs drastically in compressibility from other liquids is excluded, then the correlation parameters remain almost unchanged

$$K_0 = (-4406.40\pm144.75) + (0.9855\pm0.0086)(1000V/\Delta V) \quad (5)$$

$(R = 0.9983,\ \mathrm{SD} = 289.71,\ N = 46)$.

Note the considerable deviation from the general dependence for water for which the experimental parameters were measured very reliably. The elevated compressibility of water compared to the expected value (see Fig. 1) can be a consequence of a change in the three-dimensional structure of hydrogen bonds of water with the pressure increase.

In the present work we propose a simple method for indirect determination of the dependence of $\Delta V/V$ on $P$ by data on the absorption of a dye solution under pressure. For this purpose it is necessary that the increase in the absorbance with the pressure increase would be caused only by an increase in the number of solvent molecules per volume unit. It is well known[3,4] that the pressure increase induces the change in many characteristics of the solvent (density, refractive index, dielectric constant, viscosity, *etc.*). It was also found[3] that with the pressure increase to 100 MPa the absorption bands undergo a small (2—3 nm), usually bathochromic shift. For purposes of the present study we chose the dye Rhodamine-6G with a smooth maximum of the absorption band in the visible spectral region. It follows from the data of the absorption spectra of dye solutions in carbon tetrachloride at 298.15 K and atmospheric pressure that the molar absorption coefficient in the wavelength interval from 486 to 494 nm is rather constant (22790±60 L mol$^{-1}$ cm$^{-1}$). The spectrum in toluene almost coincides with that in carbon tetrachloride and has a plateau at 486—493 nm with the molar absorption coefficient 22 610±90 L mol$^{-1}$ cm$^{-1}$. When the pressure increases, the absorbance can change due to a change in the volume and, hence, in the concentration, and due to a change in the molar absorption coefficient. It can be checked that the molar absorption coefficient remains constant with the pressure increase only by comparison of the plots of $\Delta V/V$ *vs.* $P$ obtained from the data on the absorption of the dye solution under pressure and by direct precision measurements. The variable-volume quartz cell designed for these measurements (Fig. 2) has a rectangular cross section (1×1 cm) in the bottom part (*1*) and is cylindrical with the thoroughly grind piston (*5*) in the upper part (*2*). Volumes *1* and *2* are separated by a quartz diaphragm (*3*) with the perforated channel (*4*).

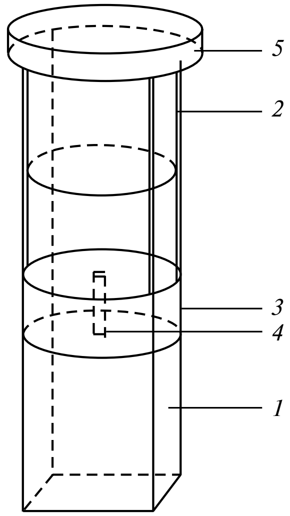

**Fig. 2.** Quartz cell of variable volume: *1*, bottom optical part of the cell (1×1×3 cm); *2*, upper part with the cylindrical section; *3*, quartz rod with the connecting channel (*4*); *5*, cylindrical plug.

In the first variant of measurements, a solution of the dye was syringed into parts *1* and *2*, closed with plug *5*, and placed in a high-pressure optical bomb in the cell compartment of the spectrophotometer.

For the all-sided compression in the working pressure interval (to 100 MPa), the change in the cell size due to compression of the quartz walls ($l$ = const) can be neglected. Then, taking into account changes in the concentration of the solution with the pressure change ($C_P/C_0 = V_0/V_P$) and accepting the absorption coefficient constant in the studied pressure interval, we have

$$D_P = D_0V_0/V_P \text{ or } \Delta V_P/V_0 = (D_P - D_0)/D_P.$$

Here $V$ and $D$ are the volume of the solution and its absorbance under atmospheric ($V_0$, $D_0$) and elevated ($V_P$, $D_P$) pressures, respectively. The obtained data (Fig. 3) for the solutions in carbon tetrachloride and toluene agree with the known dependences of $\Delta V/V$ on $P$ determined by direct methods.[3,4]

A drawback of this variant is a low sensitivity resulting in errors about ±5%. This is caused by comparatively small changes in the volume and absorption of the solvent ($D_P/D_0 \le 1.10$).

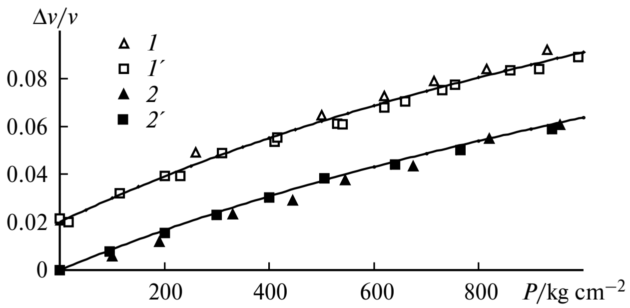

**Fig. 3.** Changes in the volume of carbon tetrachloride (*1*, *1′*) and toluene (*2*, *2′*) with the pressure increase by the data of precision measurements[3,4] (solid line) and results of calculation from the change in the absorbance of the dye solution upon compression (*1*, *2*) and pumping of the dye solution from the upper volume into the cell compartment with the solvent (*1′*, *2′*); 25 °C. The values for carbon tetrachloride are shifted along the ordinate by 0.02.

In the second, more sensitive variant of measurements, we achieved a noticeably higher change in the absorbance with the pressure increase. In this case, when the solvent is compressed by even 5%, which is really attainable for the most part of organic liquids under pressures to 100 MPa, one can observe a change in the absorption in volume *1* (see Fig. 2) by 0.525 absorbance unit, if the initial absorbance of the dye in volume *2* is 10.

For this purpose, the solvent was charged into the bottom volume *1* of the cell (see Fig. 2), then connecting channel *4* was tightly closed by a shortened (10 mm) syringe needle with an internal diameter of 0.3 mm, and a dye solution with the absorbance about 5—10 units was introduced to the upper volume (*2*), which was closed with the plug (*5*). Under elevated pressure the absorbance of the dye solution in volume *2* ($D_P{}^2$) is determined by the equation $D_P{}^2 = D_0{}^2(V_0/V_P)$. Under this pressure the solvent volume (*1*) decreases by $\Delta V_P{}^1$ because of compression, resulting in pumping of the dye solution from volume *2* into volume *1* with the solvent. The $V_P/V_0$ ratio is independent of $V_0$ and, therefore, the absorbance in volume *1* is the following:

$$D_P{}^1 = D_0{}^2(V_0{}^2/V_P{}^2)(\Delta V_P{}^1/V_0{}^1) = D_0{}^2(\Delta V_P{}^1/V_P{}^1). \qquad (6)$$

After the transform we have

$$V_P{}^1/V_0{}^1 = D_0{}^2/(D_P{}^1 + D_0{}^2), \qquad (7)$$

$$\Delta V_P/V_0 = D_P{}^1/(D_P{}^1 + D_0{}^2). \qquad (8)$$

The experimental data are shown in Fig. 3. Note that the results of the second variant of measurements of compressibility under elevated pressures are better than those of the first variant. A disadvantage of the second variant is the low rate of diffusion distribution in volume *1* of the dye solution introduced from volume *2*.

## Experimental

Rhodamine-6G was chosen because it has a plateau at the maximum of the absorption band (486—494 nm, Specord UV—Vis, tetrachloromethane, toluene). The volume-variable quartz cell was mounted in the housing of the optical unit (25±0.1 °C) to which pressure was transmitted with isooctane through a mercury seal.[7] The pressure was measured with a DM5007A-1000 pressure gauge with an accuracy of ±2 kg cm$^{-2}$.

In the first variant the absorbance was measured by stepwise compression of the solution followed by pressure discharge with an interval for thermal relaxation of ~15 min. The obtained data are described by the single dependence for both the increase and decrease in pressure.

In the second variant measurements were carried out only with the pressure increase. When vertical channels ~5 mm long on the bottom side part of plug *5* and on the upper internal surface of cylindrical section *2* are superposed (see Fig. 2), an air bubble and excess dye solution are pressed from the cell. Then plug *5* was turned by 180°. Thus assembled cell was immersed into a vessel with tetrachloromethane to wash the outer surface of the cell from dye traces and then mounted in the optical bomb. After the cell was filled, weak color ($D_0{}^1$) almost always appeared in the bottom part (*1*) of the cell upon pressing in plug *5* because of trace mixing of the solutions. In these cases, the change in the absorption in volume *1* ($(D_P{}^1)_{\mathrm{corr}}$) and the compression under elevated pressure were calculated using the equation

$$\begin{aligned}(D_P{}^1)_{\mathrm{exp}} &= (D_P{}^1)_{\mathrm{corr}} + D_0{}^1V_0/V_P = \\ &= (D_0{}^2 + D_0{}^1)V_0/V_P - D_0{}^2. \end{aligned} \qquad (9)$$

The $D_0{}^2$ value was calculated from the data on absorption of solution *2* dilute by 10—50 times. The optical unit and operation procedure have been described earlier.[7]

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## References

1. S. D. Hamann, *Ann. Rev. Phys. Chem.*, 1964, **15**, 349.
2. A. T. J. Hayward, *J. Phys. D: Appl. Phys.*, 1971, **4**, 938.
3. N. S. Isaacs, *Liquid Phase High Pressure Chemistry*, Wiley-Interscience, Chichester—New York—Brisbane—Toronto, 1981, 414 pp.
4. W. J. le Noble, *Organic High Pressure Chemistry*, Elsevier, Amsterdam—Oxford—New York—Tokyo, 1988, 489 pp.
5. V. D. Kiselev, E. A. Kashaeva, G. G. Iskhakova, L. N. Potapova, and A. I. Konovalov, *J. Phys. Org. Chem.*, 2006, **19**, 179.
6. Y. Marcus and G. T. Hefter, *J. Mol. Liquids*, 1997, **73—74**, 61.
7. V. D. Kiselev, E. A. Kashaeva, and A. I. Konovalov, *Tetrahedron*, 1999, **55**, 1153.

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